

## A 1,2,3-Triphosphabicyclo[1.1.0]butane and its [2 + 2]Cycloaddition Product with Transient 1,2,3-Triphosphabutadiene

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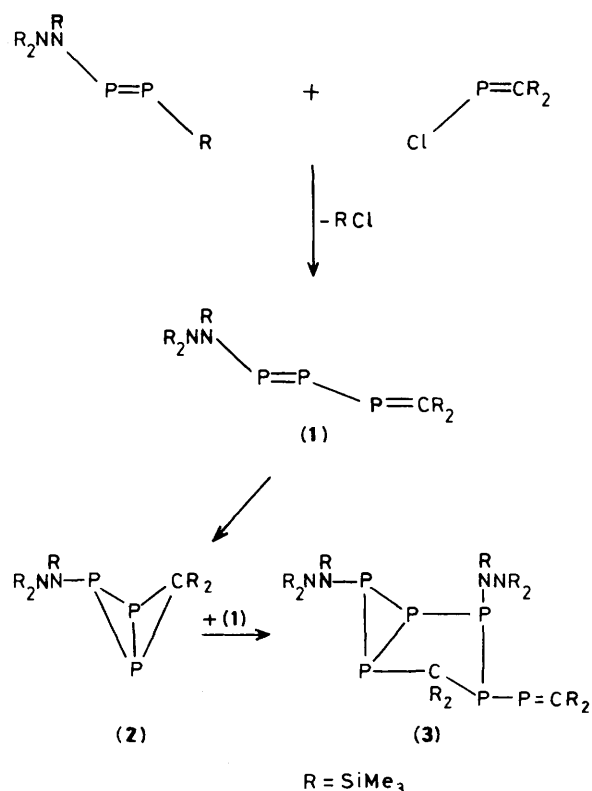
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Reaction of  $R_2NN(R)P=PR$  with  $ClP=CR_2$  ( $R = SiMe_3$ ) affords a 1,2,3-triphosphabicyclo[1.1.0]butane,  $R_2NN(R)P=P-CR_2$ , which forms a [2 + 2]cycloaddition product with a transient 1,2,3-triphosphabutadiene, the structure of which has been determined.

Phosphabutadienes in which one or more carbon atoms are replaced by dico-ordinate phosphorus atoms are of considerable interest in the chemistry of phosphorus(III) double bonded systems.<sup>1</sup> While it has been demonstrated recently that sterically non-protected species undergo isomerisations

yielding phosphacyclobutenes,<sup>2</sup> little is known about phosphabicyclobutenes,<sup>3</sup> another isomeric form of phosphabutadienes. Here we report on the synthesis of a triphosphabicyclobutane<sup>4</sup> (2) via isomerization of transient 1,2,3-triphosphabutadiene (1), and the cycloaddition of (1) and (2) with formation of (3).

Treatment of an  $Et_2O$ /pentane solution of  $RP=PNRNR_2$ <sup>5</sup> with one equivalent of  $ClP=CR_2$  ( $R = SiMe_3$ )<sup>6</sup> and a catalytic amount of hexamethylphosphoric triamide (HMPT) at 25 °C gives a mixture of the polycyclic phosphorus compounds (2) and (3). Separation of (3) was achieved by concentration of the reaction mixture and crystallization (24% yield), and (2) was obtained after vacuum distillation of the residue and crystallization from a little pentane at -30 °C (29% yield). The constitution of (2) as the unknown 1,2,3-triphosphabicyclo-



Scheme 1

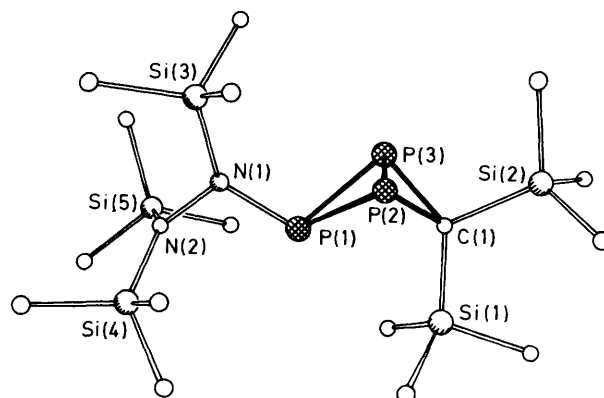


Figure 1. View of (2) with important bond lengths (Å) and angles (°): P(1)-P(2) 2.215(2), P(1)-P(3) 2.226(2), P(2)-P(3) 2.158(2), P(2)-C(1) 1.883(4), P(3)-C(1) 1.880(5), N(1)-P(1) 1.707(3), C(1)-Si(1) 1.917(5), C(1)-Si(2) 1.903(4), P(2)-P(1)-P(3) 58.2(1), P(1)-P(2)-P(3) 61.2(1), P(1)-P(3)-P(2) 60.7(1), P(2)-P(3)-C(1) 55.1(1), P(2)-C(1)-P(3) 70.0(2). Torsion angle: P(1)-P(2)-P(3)-C(1) 103.3(1)°.

clo[1.1.0]butane was shown by electron impact mass spectrometry (70 eV,  $M^+ m/z$  498) as well as by  $^{31}\text{P}$  n.m.r. ( $-6.8$  t,  $-290.7$  d p.p.m.;  $J_{\text{PP}}$  195 Hz).† We propose that (2) is formed by intramolecular ring closure of the transient 1,2,3-triphosphabutadiene (1), which is formed by elimination of chlorosilane from the starting materials (Scheme 1). The molecular structure‡ of (2) is shown in Figure 1. The molecule adopts the expected butterfly conformation [torsion angle: P(1)–P(2)–P(3)–C(1) 103.3°]. The peripheral P–P and P–C bond lengths (2.22 and 1.88 Å, respectively) are consistent with a bond order of unity, while the bridgehead bond distance (2.16 Å) is significantly shortened.§ It is worthy of note that the nearly coplanar orientation of the  $\text{sp}^2$ -hybridized nitrogen substituent at P(1) with respect to the N(1)–P(1)–C(1) plane (angle between the normals to the planes SiNN and NPC = 13°), is quite different from that of known tetraphosphabicyclobutanes.<sup>7</sup>

The second product (3) possesses the same elemental composition as (2). However in the mass spectrum the molecular ion is observed at twice the mass ( $M^+ m/z$  996) of (2) and a complex pattern is found in the  $^{31}\text{P}$  n.m.r. spectrum which exhibits six chemically non-equivalent phosphorus atoms. The n.m.r. data† are in accord with a 1,2,3,5,6-pentaphosphabicyclo[3.1.0]hexane with an exocyclic phospho-alkenyl ligand. Formation of (3) strongly suggests the existence of transient triphosphabutadiene (1), the P–P double bond of which reacts with the P–C bond of (2) via [2 + 2]cycloaddition. Similar cycloadditions are well known from bicyclobutanes,<sup>8</sup> but have not been observed so far in phosphorus chemistry. The bicyclic structure of (3) (Figure 2)

† Selected data for (2): m.p. 63–64°C;  $^1\text{H}$  n.m.r. ( $\text{C}_6\text{D}_6$ , 25°C)  $\delta$  0.13 (s, 9H,  $\text{CSiMe}_3$ ), 0.22 (s, 9H,  $\text{PNSiMe}_3$ ), 0.24 [s, 18H,  $\text{N}(\text{SiMe}_2)_2$ ];  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. ( $\text{C}_6\text{D}_6$ , 25°C)  $\delta$  2.1 (t,  $J$  4.4 Hz,  $\text{P}_2\text{CSiC}_3$ ), 2.9 [s,  $\text{N}(\text{SiC}_3)_2$ ], 3.5 (s,  $\text{CSiC}_3$ ), 7.4 (d,  $J$  12.9 Hz,  $\text{PNSiC}_3$ ). The signals for the ring carbon atoms are not observed owing to insufficient resolution.

For (3): m.p. 149–150°C;  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. ( $\text{C}_6\text{D}_6$ , 25°C)  $\delta$   $-39.9$  [P(1)],  $-91.5$  [P(2)],  $-142.2$  [P(3)],  $131.9$  [P(4)],  $25.7$  [P(5)],  $339.1$  [P(6)] p.p.m.;  $J_{\text{P(1)P(2)}}$   $-248$ ,  $J_{\text{P(1)P(3)}}$   $-196$ ,  $J_{\text{P(1)P(4)}}$   $285$ ,  $J_{\text{P(2)P(3)}}$   $-193$ ,  $J_{\text{P(2)P(6)}}$   $-14.5$ ,  $J_{\text{P(3)P(4)}}$   $226$ ,  $J_{\text{P(3)P(5)}}$   $64.5$ ,  $J_{\text{P(3)P(6)}}$   $5$ ,  $J_{\text{P(4)P(5)}}$   $-222$ ,  $J_{\text{P(4)P(6)}}$   $85.5$ ,  $J_{\text{P(5)P(6)}}$   $-248$  Hz. Further couplings were not observed owing to insufficient resolution.

‡ Crystal data for (2):  $\text{C}_{16}\text{H}_{45}\text{N}_2\text{P}_3\text{Si}_5$ ,  $M = 498.9$ , monoclinic, space group  $P2_1c$ , yellowish crystals out of pentane, dimensions  $0.2 \times 0.2 \times 0.3$  mm<sup>3</sup>,  $a = 9.865(4)$ ,  $b = 27.857(8)$ ,  $c = 11.469(4)$  Å,  $\beta = 104.65(3)^\circ$ ,  $U = 3.049$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.09$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.39$  mm<sup>-1</sup>. 5370 Symmetry independent reflections ( $2\theta_{\text{max.}} = 50^\circ$ ), 3586 reflections with  $|F| > 4\sigma(F)$  were used for the structure solution (direct methods) and refinement (235 parameters), non hydrogen atoms were refined anisotropically, H-atoms localized by difference electron density determination and refined using a 'riding' model,  $R = 0.060$  ( $R_w = 0.061$ ,  $w^{-1} = \sigma^2(F) + 0.0006 F^2$ ).

For (3):  $\text{C}_{32}\text{H}_{90}\text{N}_4\text{P}_6\text{Si}_{10} \cdot 1/2 \text{C}_3\text{H}_{12}$ ,  $M = 1033.8$ , triclinic, space group  $P1$ , reddish brown crystals out of pentane, dimensions  $0.2 \times 0.4 \times 0.4$  mm<sup>3</sup>,  $a = 9.640(5)$ ,  $b = 16.847(7)$ ,  $c = 20.316(8)$  Å,  $\alpha = 96.79(3)^\circ$ ,  $\beta = 97.41(4)^\circ$ ,  $\gamma = 102.04(4)^\circ$ ,  $U = 3.164$  nm<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.08$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.38$  mm<sup>-1</sup>. 8265 Symmetry independent reflections ( $2\theta_{\text{max.}} = 45^\circ$ ), 6521 with  $|F| > 4\sigma(F)$  used for structure solution (direct methods) and refinement (481 parameters), non-hydrogen atoms were refined anisotropically (solvent carbon atoms isotropically), H atoms localized by difference electron density determination and refined using a 'riding' model,  $R = 0.051$  ( $R_w = 0.053$ ,  $w^{-1} = \sigma^2(F) + 0.0007 F^2$ ).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Worthy of note are the relatively long C–Si bond lengths [1.903(4)–1.943(4) Å for the ring-bonded  $\text{CSi}_2$  fragment in (2) and (3)].

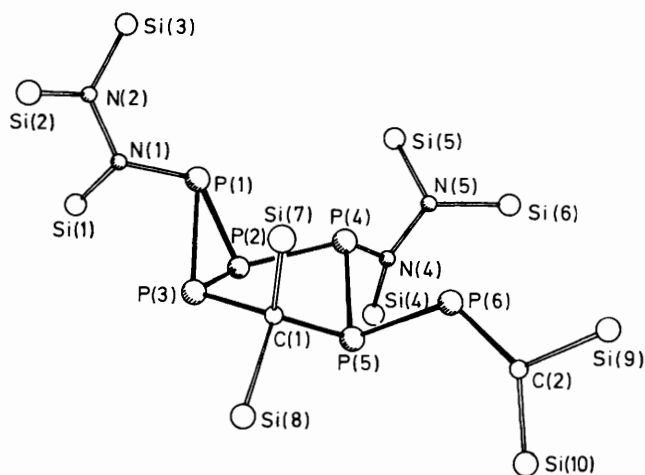


Figure 2. View of (3) (without Me groups) with important bond lengths (Å) and angles (°): P(1)–P(2) 2.201(2), P(1)–P(3) 2.262(1), P(2)–P(3) 2.183(1), P(2)–P(4) 2.251(2), P(3)–C(1) 1.909(4), P(4)–P(5) 2.271(1), P(5)–C(1) 1.891(4), P(5)–P(6) 2.247(2), P(6)–C(2) 1.675(4), C(1)–Si(7) 1.919(4), C(1)–Si(8) 1.943(4), P(2)–P(1)–P(3) 58.5(1), P(1)–P(3)–P(2) 59.3(1), P(1)–P(2)–P(3) 62.1(1), P(1)–P(2)–P(4) 89.9(1), P(2)–P(4)–P(5) 90.6(1), P(1)–P(3)–C(1) 112.5(1), P(3)–C(1)–P(5) 108.6(2), P(4)–P(5)–C(1) 97.2(1), P(5)–P(6)–C(2) 112.7(2).

is further confirmed by X-ray crystal determination.‡§ The molecule exhibits the sterically favoured envelope conformation with a *trans*-arrangement of the phosphorus substituents, which has also been shown for the hexaphosphabicyclo[3.1.0]hexane.<sup>9</sup>

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